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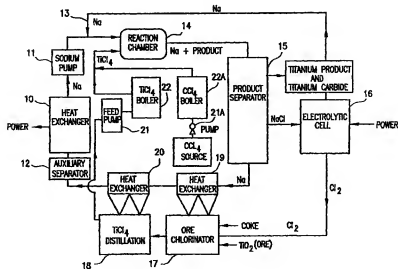
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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: METAL MATRIX WITH CERAMIC PARTICLES DISPERSED THEREIN



(57) Abstract: A metal matrix having ceramic particles distributed therein is made by the process of introducing a halide vapor of the metal forming the matrix into flowing alkali or alkaline earth metal or mixtures thereof. A vapor of the constituents of the ceramic. Sufficient excess alkali and/or alkaline earth metal is present to maintain the temperature of substantially all of the reaction products below the sintering temperatures to produce metal matrix particles and ceramic particles and salt particles in excess alkali and/or alkaline earth metal. The excess alkali and/or alkaline earth metal and the salt particles are removed leaving a mixture of metal matrix particles and ceramic particles. A method is also disclosed.

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METAL MATRIX WITH CERAMIC PARTICLES DISPERSED THEREIN

FIELD OF THE INVENTION

This invention relates to compositions and methods of making same in which a metal matrix powder or particulates have distributed there through ceramic particles or particulates and solid objects made therefrom. The invention makes use of the Armstrong Process which is disclosed in U.S. patent nos. 6,409,797; 5,958,106; 5,779,761 and 6,861,038, all of the disclosures of which are incorporated herein by reference.

BACKGROUND OF THE INVENTION

Metallic matrices having ceramic particles distributed throughout are used in a significant number of industries. For instance, tungsten carbide is a very hard material and can be incorporated into various metal matrices to provide abrading materials, whereas titanium nitride and/or titanium carbides may be incorporated into a titanium matrix for use as cylinder liners in aluminum block engines.

In general, inorganic powder/particle manufacture has traditionally been made in a number of ways, comunion of solid metal, precipitation from a salt solution, thermal decomposition of a chemical compound, reduction of a compound, electrodeposition and the atomization of molten metals.

In general, atomization is used to produce spherical particles and brittle materials such as metal hydrides may be pulverized mechanically in ball mills and other known processes. Thermal decomposition of a chemical compound is used in some cases, such as nickel carbonyl. Some iron powders are also made this way.

With the advent of the Armstrong Process, the making of metal powders has been facilitated by the use of a liquid stream of alkali or alkaline earth metal into which is introduced a gaseous halide or a combination of halides under reducing conditions to make a metal or an alloy thereof, all as disclosed in the previously mentioned patents. The Armstrong Process can also be used to make ceramics, also set forth in above enumerated patents. Various commercial metals have been made with the Armstrong Process, most noticeably commercial pure (CP) titanium and 6/4 titanium meeting the ASTM grade 5 qualifications. However, there is a need

for compositions of metal or metal powder having ceramic particles or powder distributed throughout.

SUMMARY OF THE INVENTION

Accordingly, it is a principal object of the present invention to provide a composition of matter comprising a metal matrix having ceramic particles distributed therein made by the process of introducing a halide of the metal forming the matrix into flowing alkali or alkaline earth metal or mixtures thereof, introducing a source of the constituents of the ceramic into flowing alkali or alkaline earth metal or mixtures thereof, wherein sufficient excess alkali and/or alkaline earth metal is present to maintain the temperature of substantially all of the reaction products below the sintering temperature thereof to produce metal matrix particles and ceramic particles and salt particles in excess alkali and/or alkaline earth metal, and removing the excess alkali and/or alkaline earth metal and the salt particles leaving a mixture of metal matrix particles and ceramic particles.

Another object of the present invention is to provide a composition of matter comprising a metal matrix having ceramic particles less than about one micron in average diameter distributed therein made by the process of introducing a chloride of the metal or metals forming the matrix into flowing alkali or alkaline earth metal or mixtures thereof, introducing a source of the constituents of the ceramic into flowing alkali or alkaline earth metal or mixtures thereof, wherein sufficient excess alkali and/or alkaline earth metal is present to maintain the temperature of substantially all of the reaction products below the sintering temperature thereof to produce metal matrix particles and ceramic particles and salt particles in excess alkali and/or alkaline earth metal, and wherein the boiling points of the chlorides are less than about 500°C, and removing the excess alkali and/or alkaline earth metal and the salt particles leaving a mixture of metal matrix particles and ceramic particles.

A final object of the invention is to provide a method of making a composition having a metal matrix powder with ceramic particles distributed therein, the method comprising establishing a stream of liquid alkali or alkaline earth metal or mixtures thereof, introducing halide vapor of the metal matrix and a source of a non-metal constituent of the ceramic particles at not less than sonic velocity into the liquid alkali or alkaline earth metal stream, the liquid alkali or alkaline earth metal being present

in sufficient quantity to maintain substantially all of the reaction products below the sintering temperatures thereof.

The invention consists of certain novel features and a combination of parts hereinafter fully described, illustrated in the accompanying drawings, and particularly pointed out in the appended claims, it being understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

For the purpose of facilitating an understanding of the invention, there is illustrated in the accompanying drawings a preferred embodiment thereof, from an inspection of which, when considered in connection with the following description, the invention, its construction and operation, and many of its advantages should be readily understood and appreciated.

FIGURE 1 is a process flow diagram showing the continuous process as an example titanium metal from titanium tetrachloride and a ceramic particulate mixed therewith; and

FIG. 2 is an example of a typical burner reaction chamber for the process disclosed in Figure 1.

DETAILED DESCRIPTION OF THE INVENTION

The process of the invention may be practiced with the use of any alkali or alkaline earth metal depending upon the metal or non-metal to be reduced. In some cases, combinations of an alkali or alkaline earth metals may be used. Moreover, any halide or combinations of halides may be used with the present invention although in most circumstances chlorine, being the cheapest and most readily available, is preferred. Of the alkali or alkaline earth metals, by way of example, sodium will be chosen not for purposes of limitation but merely purposes of illustration, because it is cheapest and preferred, as has chlorine been chosen for the same purpose, but magnesium is also commercially available.

Regarding the non-metals or metals to be reduced, it is possible to reduce a single metal such as titanium or tantalum or zirconium, selected from the list set forth hereafter. It is also possible to make alloys of a predetermined composition by providing mixed metal halides at the beginning of the process in the required

molecular ratio. By way of example, Table 1 sets forth heats of reaction per gram of liquid sodium for the reduction of a stoichiometric amount of a vapor of a non-metal or metal halides applicable to the Inventive process.

TABLE 1

FEEDSTOCK	HEAT kJ/g
TiCl ₄	10
AlCl ₃	9
SiCl ₄	11
SnCl ₂	4
SbCl ₃	14
BeCl ₂	10
Bcl ₃	12
TaCl ₅	11
ZrCl ₄	9
VCl ₄	12
NbCl ₅	12
MoCl ₄	14
GaCl ₃	11
UF ₆	10
ReF ₆	17

Ceramic particles which are useful in the present invention may have a metal constituent selected from one or more of W, B, Bi, Fe, Gd, Ge, Hf, In, Pb, Sn, Zr, and these ceramics may be in the form of a nitride, a carbide, a phosphide, a sulfide, a boride or mixtures thereof.

It is best if the vapor introduced into the flowing metal stream has a boiling point of not greater than about 500°C, merely for purposes of using less expensive materials in the apparatus necessary to practice the invention. Sources of various materials useful in the present invention to provide ceramic particles are carbon

tetrachloride which has a boiling point of around 76.7°C; N₂; PCl₃ with a boiling point of about 76°C; SCl₂ with a boiling point of about 60°C; BCl₃ with a boiling point of about 13°C, where a halide is not useful for whatever reason, the element itself may be used in some cases, for instance, phosphorous sublimates at 417°C and sulfur boils at 445°C. Of course nitrogen is a gas at room temperature.

Various metallic components of ceramic parts such as for instance, tungsten tetrachloride with a boiling point of about 346°C may be used as well as other chlorides, fluorides or bromides, as is well known in the art. The compositions useful in the present invention depend on the end use thereof and the matrix may be as low as about 5% by weight or as high as 95% by weight, depending on the end use.

The process will be illustrated, again for purposes of illustration and not for limitation, with a single metal titanium being produced from the tetrachloride for the matrix material and TiC produced with CCl₄ for the ceramic.

A summary process flowsheet is shown in FIG. 1. Sodium and titanium tetrachloride are combined in a reaction chamber 14 where titanium tetrachloride vapor from a source thereof in the form of a boiler 22 is injected within a flowing sodium stream from a continuously cycling loop thereof including a sodium pump 11. Carbon tetrachloride from a source thereof is pumped by pump 21A to a boiler 22A and there to the line from boiler 22 to the reaction chamber 14. The sodium stream is replenished by sodium provided by an electrolytic cell 16. The reduction reaction in chamber 14 is highly exothermic, forming molten reaction products of titanium and sodium chloride with titanium carbide particles. Since TiC has a melting point in excess of 3000°, TiC particles when made are solid, not molten. The molten reaction products are quenched in the bulk sodium stream. Particle sizes and reaction rates are controlled by metering of the titanium tetrachloride vapor carbon tetrachloride flowrates (by controlling the supply pressure), dilution of the titanium tetrachloride vapor with an inert gas, such as He or Ar, and the sodium flow characteristics and mixing parameters in the reaction chamber which includes a nozzle for the titanium tetrachloride mixed with carbon tetrachloride and a surrounding conduit for the liquid sodium. The vapor is intimately mixed with the liquid in a zone enclosed by the liquid, i.e., a liquid continuum, and the resultant temperature, significantly affected by the heat of reaction, is controlled by the

quantity of flowing sodium and maintained below the sintering temperature of the produced metal, such as for titanium at about 1000 degree C. The ratio of Ti metal to TiC is controlled by flow controllers, not shown, providing adjustment of the gases flowing into reaction chamber 14. Preferably, the temperature of the sodium away from the location of halide introduction is maintained in the range of from about 200 degree C. to about 600 degree C. Products leaving the reaction zone are quenched in the surrounding liquid before contact with the walls of the reaction chamber and preferably before contact with other product particles. This precludes sintering and wall erosion.

The surrounding sodium stream then carries the titanium and titanium carbide and sodium chloride reaction products away from the reaction region. These reaction products are removed from the bulk sodium stream by conventional separators 15 such as cyclones, particulate filters, magnetic separators or vacuum stills, with vacuum distillation being preferred.

Three separate options for separation of the titanium and titanium carbide from the sodium chloride exist. The first option removes the titanium/titanium chloride and sodium chloride products in separate steps. This is accomplished by maintaining the bulk stream temperature such that the titanium/titanium carbide product is solid but the sodium chloride is molten through control of the ratio of titanium tetrachloride and sodium flowrates to the reaction chamber 14. For this option, the titanium/titanium carbide product is removed first, the bulk stream cooled to solidify the sodium chloride, then the sodium chloride is removed from separator 12.

In the second option for reaction product removal, a lower ratio of titanium tetrachloride to sodium flowrate would be maintained in the reaction chamber 14 so that the bulk sodium temperature would remain below the sodium chloride solidification temperature. For this option, titanium/titanium carbide product and sodium chloride would be removed simultaneously using conventional separators. The sodium chloride and any residual sodium present on the particles would then be removed in a water-alcohol wash.

In the third, and preferred option for product removal, the solid cake of salt, Ti/TiC product and Na is vacuum distilled to remove the Na. Thereafter, the Ti/TiC product is passivated by passing a gas containing some O₂ over the mixture of salt

and Ti/TiC product followed by a water wash to remove the salt leaving Ti/TiC product with surfaces of TiO_2 , which can be removed by conventional methods, if required.

Following separation, the sodium chloride is then recycled to the electrolytic cell 16 to be regenerated. The sodium is returned to the bulk process stream for introduction to reaction chamber 14 and the chlorine is used in the ore chlorination 17. It is important to note that while both electrolysis of sodium chloride and subsequent ore chlorination will be performed using technology well known in the art, such integration and recycle of the reaction by-product directly into the process is not possible with the Kroll or Hunter process because of the batch nature of those processes and the production of titanium sponge as an intermediate product. In addition, excess process heat is removed in heat exchanger 10 for co-generation of power. The integration of these separate processes enabled by the inventive chemical manufacturing process has significant benefits with respect to both improved economy of operation and substantially reduced environmental impact achieved by recycle of both energy and chemical waste streams.

Chlorine from the electrolytic cell 16 is used to chlorinate titanium ore (utile, agnates or ilmenite) in the chlorination 17. In the chlorination stage, the titanium ore is blended with coke and chemically converted in the presence of chlorine in a fluidized-bed or other suitable kiln chlorination. The titanium dioxide contained in the raw material reacts to form titanium tetrachloride, while the oxygen forms carbon dioxide with the coke. Iron and other impurity metals present in the ore are also converted during chlorination to their corresponding chlorides. The titanium chloride is then condensed and purified by means of distillation in column 18. With current practice, the purified titanium chloride vapor would be condensed again and sold to titanium manufacturers; however, in this integrated process, the titanium tetrachloride vapor stream is used directly in the manufacturing process via a feed pump 21 and boiler 22.

After providing process heat for the distillation step in heat exchangers 19 and 20, the temperature of the bulk process stream is adjusted to the desired temperature for the reaction chamber 14 at heat exchanger 10, and then combined with the regenerated sodium recycle stream, and injected into the reaction chamber.

The recovered heat from heat exchangers 19 and 20 may be used to vaporize liquid halides from the sources thereof to produce halide vapor to react with the metal or the non-metal. It should be understood that various pumps, filters, traps, monitors and the like will be added as needed by those skilled in the art.

In all aspects, for the process of FIG. 1, it is important that the titanium that is removed from the separator 15 be at or below the sintering temperature of titanium in order to preclude and prevent the solidification of the titanium on the surfaces of the equipment and the agglomeration of titanium particles into large masses, which is one of the fundamental difficulties with the commercial processes used presently. By maintaining the temperature of the titanium metal below the sintering temperature of titanium metal, the titanium will not attach to the walls of the equipment or itself as it occurs with prior art and, therefore, the physical removal of the same will be obviated. This is an important aspect of this invention and is obtained by the use of sufficient sodium metal or diluent gas or both to control the temperature of the elemental (or alloy) and ceramic product. In other aspects, FIG. 1, is illustrative of the types of design parameters which may be used to produce titanium particles/titanium carbide particles in a continuous process which avoids the problems with the prior art, and produces a more uniform distribution of ceramic particles.

Referring now to FIG. 2, there is disclosed a typical reaction chamber in which a choke flow or injection nozzle 23, completely submerged in a flowing liquid metal stream, introduces the halide vapors from boilers 22 and 22A in a controlled manner into the liquid metal reductant stream 13. The reaction process is controlled through the use of a choke-flow (sonic or critical flow) nozzle. A choke-flow nozzle is a vapor injection nozzle that achieves sonic velocity of the vapor at the nozzle throat. That is the velocity of the vapor is equal to the speed of sound in the vapor medium at the prevailing temperature and pressure of the vapor at the nozzle throat. When sonic conditions are achieved, any change in downstream conditions that causes a pressure change cannot propagate upstream to affect the discharge. The downstream pressure may then be reduced indefinitely without increasing or decreasing the discharge. Under choke flow conditions only the upstream conditions need to be controlled to control the flow-rate. The minimum upstream pressure

required for choke flow is proportioned to the downstream pressure and termed the critical pressure ratio. This ratio may be calculated by standard methods.

The choke flow nozzle serves two purposes: (1) it isolates the vapor generator from the liquid metal system, precluding the possibility of liquid metal backing up in the halide feed system and causing potentially dangerous contact with the liquid halide feedstock, and (2) it delivers the vapor at a fixed rate, independent of temperature and pressure fluctuations in the reaction zone, allowing easy and absolute control of the reaction kinetics.

The liquid metal stream also has multiple functional uses: (1) it rapidly chills the reaction products, forming product powder without sintering, (2) it transports the chilled reaction products to a separator, (3) it serves as a heat transfer medium allowing useful recovery of the considerable reaction heat, and (4) it feeds one of the reactants to the reaction zone.

For instance in FIG. 2, the sodium 13 entering the reaction chamber may be at 200.degree. C. having a flow rate of 38.4 kilograms per minute. The titanium tetrachloride from the boiler 22 may be at 2 atmospheres and at a temperature of 164.degree. C., the flow rate through the line may be 1.1 kg/min. Higher pressures may be used, but it is important that back flow be prevented, so the minimum pressure should be above that determined by the critical pressure ratio for sonic conditions, or about two times the absolute pressure of the sodium stream (two atmospheres if the sodium is at atmospheric pressure) is preferred to ensure that flow through the reaction chamber nozzle is critical or choked.

The subject process may also be used to provide a mixed powder of alloy and ceramic particles and to that end, the Armstrong Process has been used to make a 6/4 titanium alloy with ASTM definitions, that is 6% aluminum, 4% vanadium, the balance titanium and this alloy may also be produced by the Armstrong Process and have ceramic particles incorporated therein according to the present invention.

As has been stated before, the equipment used to produce the 6/4 alloy is substantially as disclosed in the aforementioned patents disclosing the Armstrong Process with the exception that instead of only having a titanium tetrachloride boiler 22 as illustrated in those patents, there is also a vanadium tetrachloride boiler and an aluminum trichloride boiler which are connected to the reaction chamber by suitable

valves. The piping acts as a manifold so that the gases are completely mixed as they enter the reaction chamber and are introduced subsurface to the flowing liquid sodium. It was determined during production of the 6/4 alloy that aluminum trichloride is corrosive and required special materials not required for handling either titanium tetrachloride or vanadium tetrachloride. Therefore, Hastelloy C-276 was used for the aluminum trichloride boiler and the piping to the reaction chamber.

During most of the runs the steady state temperature of the reactor was maintained at about 400°C by the use of sufficient excess sodium. Other operating conditions for the production of the alloy were as follows:

A device similar to that described in the incorporated Armstrong patents was used except that a VCl_4 boiler and AlCl_3 boiler were provided and both gases were fed into the line feeding TiCl_4 into the liquid Na. The boiler pressures and system parameters are listed hereafter.

Experimental Procedure:

TiCl_4 Boiler Pressure = 500 kPa

VCl_4 Boiler Pressure = 630 kPa

AlCl_3 Boiler Pressure = 830 kPa

Inlet Na temperature = 240°C

Reactor Outlet Temperature = 510 C

Na Flowrate = 40 kg/min

TiCl_4 Flowrate = 2.6 kg/min

For this specific experiment, a 7/32" nozzle was used in the reactor to meter the mix of metal chloride vapors. A .040" nozzle was used to meter the AlCl_3 and a .035" nozzle was used to meter the VCl_4 into the TiCl_4 stream. The reactor was operated for approximately 250 seconds injecting approximately 11 kg of TiCl_4 . The salt and titanium alloy solids were captured on a wedge wire filter and free sodium metal was drained away. The product cake containing titanium alloy, sodium chloride and sodium was distilled at approximately 100 milli - torr at 550 to 575°C vessel wall temperatures for 20 hours. Once all the sodium metal was removed via distillation, the trap was re-pressurized with argon gas and heated to 750°C and held at temperature for 48 hours. The vessel containing the salt and titanium alloy cake was cooled and the cake was passivated with a 0.7 wt % oxygen/argon mixture.

After passivation, the cake was washed with deionized water and subsequently dried in a vacuum oven at less than 100°C.

For instance, titanium carbide may be incorporated into a 6/4 alloy simply by including in the gas injected into the flowing sodium, a specified amount of carbon tetrachloride from boiler 22A, whereas a boride may be used by injecting into the flowing sodium, a specified amount of boron trichloride. Other ceramic particles may be produced from feed stocks as before described. As is seen, therefore, a wide variety of ceramic particles may be distributed in a metal matrix by using the Armstrong Process. Preferably, but not necessarily, the metal matrix incorporates at least one metal of the ceramic particle, but the invention is not so limited. The thermodynamics of the various reactions will determine what ceramic particles can be introduced into what matrix particles, but in general, the preferred ceramics are nitrides, phosphide, sulfides and carbides. Oxides are not preferred with titanium as the oxide would react with the titanium.

After the powder is made, a wide variety of processes may be used to make solid articles therefrom and these processes are widely known and commonly used in the powder metallurgy art and include casting, press and sinter and well as many others including arc melting and the like.

While the invention has been particularly shown and described with reference to a preferred embodiment hereof, it will be understood by those skilled in the art that several changes in form and detail may be made without departing from the spirit and scope of the invention.

WHAT IS CLAIMED IS:

1. A composition of matter comprising a metal matrix having ceramic particles distributed therein made by the process of introducing a halide of the metal forming the matrix into flowing alkali or alkaline earth metal or mixtures thereof, introducing a source of the constituents of the ceramic into flowing alkali or alkaline earth metal or mixtures thereof, wherein sufficient excess alkali and/or alkaline earth metal is present to maintain the temperature of substantially all of the reaction products below the sintering temperature thereof to produce metal matrix particles and ceramic particles and salt particles in excess alkali and/or alkaline earth metal, and removing the excess alkali and/or alkaline earth metal and the salt particles leaving a mixture of metal matrix particles and ceramic particles.
2. The composition of matter of claim 1, wherein the boiling point of the halides is less than about 500°C.
3. The composition of matter of claim 1, wherein said metal matrix is one or more of Ti, Al, Sb, Be, B, Ta, V, Nb, Mo, Ga, U, Re, Zr, Si, and alloys thereof.
4. The composition of matter of claim 1, wherein said ceramic particles have a metal constituent selected from W, B, Bi, Cr, Fe, Gd, Ge, Hf, In, Pb, Sn, Zr, and mixtures or alloys thereof.
5. The composition of matter of claim 1, wherein said ceramic is a nitride, a carbide, a phosphide, a sulfide, a boride or mixtures thereof.
6. The composition of matter of claim 1, wherein said halide is a chloride.
7. The composition of matter of claim 1, wherein said metal matrix is Ti or an alloy thereof.
8. The composition of matter of claim 7, wherein said metal matrix is an aluminum and vanadium alloy of titanium.
9. The composition of matter of claim 1, wherein said halide is introduced into said flowing metal at greater than sonic velocity.
10. The composition of matter of claim 1, wherein said flowing metal is Na or Mg.
11. A solid article made from the composition of matter of claim 1.
12. A composition of matter comprising a metal matrix having ceramic particles less than about one micron in average diameter distributed therein made by

the process of introducing a chloride of the metal or metals forming the matrix into flowing alkali or alkaline earth metal or mixtures thereof, introducing a source of the constituents of the ceramic into flowing alkali or alkaline earth metal or mixtures thereof, wherein sufficient excess alkali and/or alkaline earth metal is present to maintain the temperature of substantially all of the reaction products below the sintering temperature thereof to produce metal matrix particles and ceramic particles and salt particles in excess alkali and/or alkaline earth metal, and wherein the boiling points of the chlorides are less than about 500°C, and removing the excess alkali and/or alkaline earth metal and the salt particles leaving a mixture of metal matrix particles and ceramic particles.

13. The composition of matter of claim 12, wherein said metal matrix is one or more of Ti, Al, Sb, Be, B, Ta, V, Nb, Mo, Ga, U, Re, Zr, Si, and alloys thereof.

14. The composition of matter of claim 13, wherein said ceramic is a nitride, a carbide, a phosphide, a sulfide, a boride or mixtures thereof.

15. The composition of matter of claim 14, wherein said ceramic particles have a metal constituent selected from W, B, Bi, Cr, Fe, Gd, Ge, Hf, In, Pb, Pt, Sn, Zr, and mixtures or alloys thereof.

16. The composition of matter of claim 15, wherein said metal matrix is Ti or an alloy thereof.

17. The composition of matter of claim 16, wherein said ceramic particles include a carbide and/or a nitride.

18. The composition of matter of claim 16, wherein said ceramic particles include a boride.

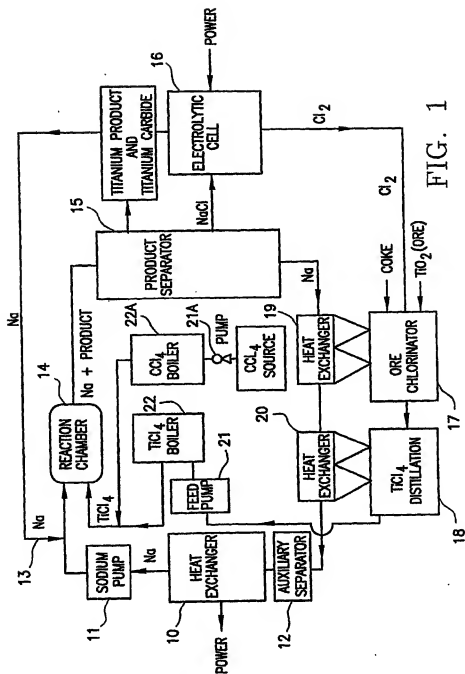
19. The composition of matter of claim 12, wherein the metal constituent of the ceramic is the same as said metal matrix.

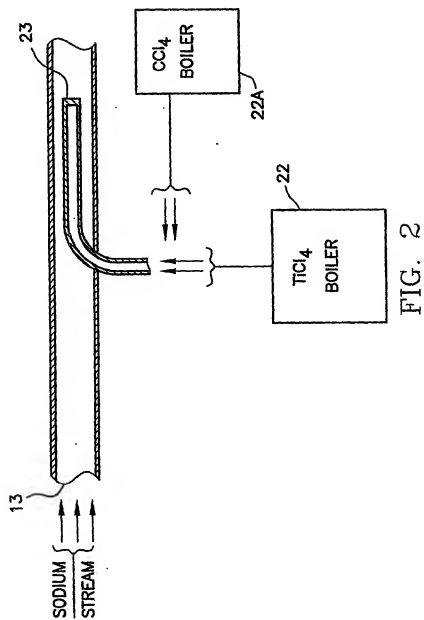
20. A solid article made from the composition of matter of claim 12.

21. A method of making a composition having a metal matrix powder with ceramic particles distributed therein, said method comprising establishing a stream of liquid alkali or alkaline earth metal or mixtures thereof, introducing halide vapor of the metal matrix and a source of a non-metal constituent of the ceramic particles at not less than sonic velocity into the liquid alkali or alkaline earth metal stream, the liquid alkali or alkaline earth metal being present in sufficient quantity to maintain

substantially all of the reaction products below the sintering temperatures thereof.

22. The method of claim 21, and further comprising forming the composition of powder into a solid article.





INTERNATIONAL SEARCH REPORT

International application No
PCT/US2007/000521

A. CLASSIFICATION OF SUBJECT MATTER
INV. B22F9/28 C22C32/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 441 039 A (GEN ELECTRIC [US]) 28 July 2004 (2004-07-28) column 5, line 11 - line 13 column 6, line 45 - line 46 paragraph [0023] - paragraph [0025] figure 3	1-22
X	WO 98/24575 A (DYNAMET TECHNOLOGY [US]) 11 June 1998 (1998-06-11) abstract	1,3-5,7, 8,11, 13-20
X	JP 05 078762 A (SUMITOMO LIGHT METAL IND) 30 March 1993 (1993-03-30) abstract	1,3-5,7, 11,13-20
-/-		

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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X document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search

15 May 2007

Date of mailing of the international search report

25/05/2007

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Morra, Valentina

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2007/000521

D(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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